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Photochromic Behaviour of Non-transition Metal Chelate Complexes of Salicylaldimines

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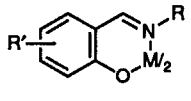
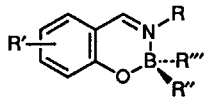
Bis(*N*-alkylsalicylaldiminato)zinc(II) and the beryllium(II) complexes **1**, as well as 5,6-benzo-1,3,2-oxazaborines **2**, display photochromic behaviour in solution, while undergoing thermally-irreversible photocoloration reactions in bulky amorphous films.

Whereas the synthesis, structure and stereodynamics of type **1** and **2** tetrahedral non-transition metal chelate compounds have been broadly covered in the literature,[1–3] their photochemical behaviour has received almost no attention.

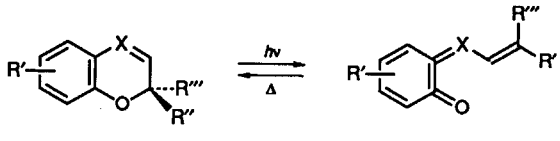


1 M = Be, Zn, Cd, Hg, Pb



2

The isoelectronic structural analogues of **1** and **2**, 2*H*-chromenes **3**, spiropyrans and spirooxazines (both containing 2*H*-chromene or 2*H*-3-azachromene moieties spiro-conjugated through the tetrahedral carbon atom) have long been known to be highly efficient photochromic compounds due to the reversible photocoloration reaction initiated by UV-irradiation.[4,5]



3a **3b** X = CH, N

It has been shown by MNDO calculations[6] that the shape of the frontier MOs and the origin of the lowest excited states in **1** and **3** are similar. The similarity was also stressed in the orbital nature of spiro-1,3-oxazines **3a** (X = N,R″,R‴-cycle) and benzo-1,3,2-oxazaborines **2**.[7] One may, therefore, expect M–O bond cleavage to readily occur in the complexes **1** and **2** in the first singlet excited state, as is the case for 2*H*-chromenes **3** and most spiropyrans and spirooxazines.[4,8,9]

Here we report on the discovery of photochromic behaviour in a systematic series of type **1** and **2** main-group metal-chelate complexes that have been studied by means of millisecond lamp-flash spectroscopy. Recently, photochromic transformation has been observed employing lamp-flash photolysis for the uranium(II) dioxide bis-chelate complex of

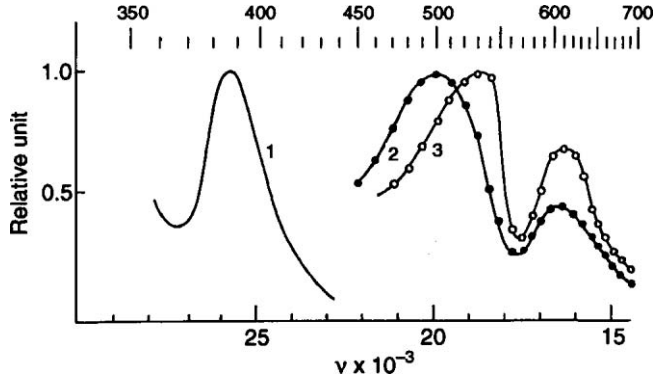


Fig. 1 Electron absorption spectra of bis(*N*-isopropylsalicylaldiminato)zinc(II) (no. 1 in Table 1) in toluene solution: (1) before irradiation; (2) after (2×10^{-4} s) one-pulse irradiation by the light of a xenon (IFPP–7000) lamp; (3) 30 ms after switching off the pulse.

N-salicyl-4-hydroxy-3,5-dimethylaniline **1** (M = UO_2, R′ = 3,5-Me_2-4-OH)[10] whose spectral properties and isomerization kinetics were found to bear a striking similarity to those of the ligand. Earlier work has also been done[11] on the photocoloration under UV-radiation (high pressure mercury lamp) of the frozen solutions (77 K, isopropanol–isopentane) of bis(salicylaldiminato)zinc(II) **1** (M = Zn, R = Ph), with the emerging long-wave absorption at 470 nm disappearing on increasing the temperature.

As seen from Figs. 1–3 (see also Table 1), the electron absorption spectra of complexes **1** and **2** consist of two long-wave bands in the region of 350–430 nm. Both the position of the absorption maxima and the intensities of the absorption bands are little affected by the origin of the metal centre M, whereas benzoannelation (R′ = benzo) leads to a 5–10 nm bathochromic shift of these bands.

Irradiation of toluene or methanol solutions of complexes **1** and **2** by the light of a xenon photolytic lamp results in the immediate coloration of the solutions due to the appearance of new long-wave absorption bands in the spectral region of 440–660 nm, see Figs. 1–3 and Table 1. The coloured forms

Table 1 Absorption spectra (λ_{max}/nm) of the metal chelate complexes **1** and **2** (R = Pr^i) and their photoisomers (obtained during lamp flash photolysis) in solution ($c = 2 \times 10^{-5}$ mol dm^{-3}) and thin solid polydispersive films

No.	Complex				Toluene		Methanol		Solid film	
	Type	M	R′	R″	Before	After	Before	After	Before	After
					318	448	260	466		
1	1	Zn	H	—	372	495	272[a]	600	380	—
						600	363			
					365	439	265	448		
2	1	B	H	—		502	352	582	—	—
						608				
					299	500	281	456		
3	2	Be	H	C_6H_4OMe-*o*	385	602	390	580	382	482
								616		680
					397	450	322	438		
4	1	Zn	4,5-Benzo	—	414	*b*	384[a]	465	—	—
							405	548		
					320	452	322	470	390	
5	1	Zn	5,6-Benzo	—	378	*b*	384	*b*	415	685
					403		406			
					320		320	458		
6	1	Be	4,5-Benzo	—	383	490	430	525	422	—
					402	572				
					319		322			
7	1	Be	5,6-Benzo	—	383[a]	450	384[a]	481	426	—
					402	556	405	559		
						458	330	465		
8	2	B	4,5-Benzo	C_6H_4OMe-*o*	420	556	440	532	415	—
								570		
					334	441	290	460		500
9	2	B	5,6-Benzo	C_6H_4OMe-*o*	405	467	430	489	405	628
						551		630		

[a] Shoulder. [b] Not registered because of the shortness of the lifetime ($< 10^{-4}$ s).

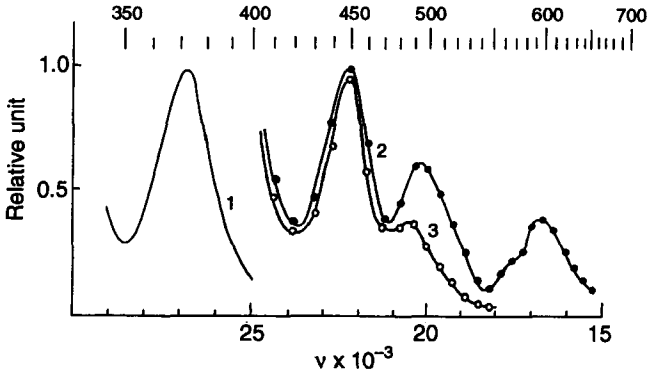


Fig. 2 Electron absorption spectra of bis(*N*-isopropylsalicylaldiminato)beryllium(II) (no. 2 in Table 1) in toluene solution: (1) before irradiation; (2) after (2×10^{-4}s) one-pulse irradiation by the light of a xenon (IFPP–7000) lamp; (3) 20 ms after switching off the pulse.

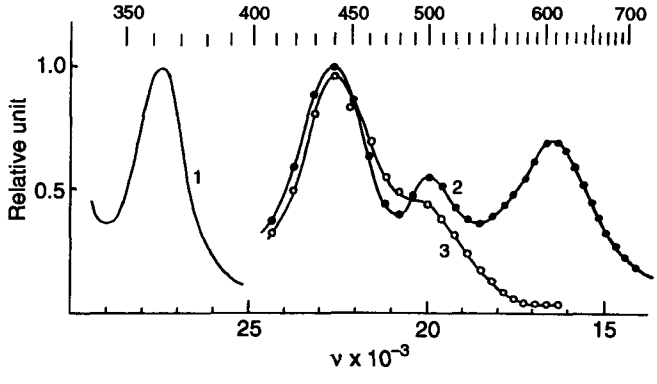


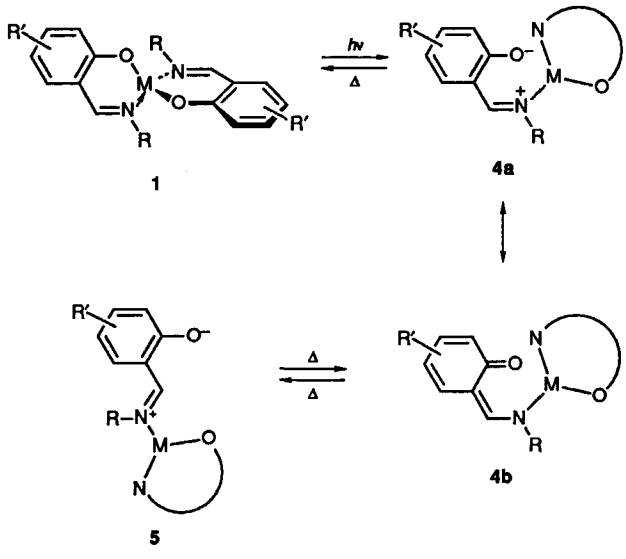
Fig. 3 Electron absorption spectra of 5,6-benzo-(2-phenyl-2-*o*-methylphenyl-3-isopropyl)-1,3,2-oxazaborine (no.3 in Table 1) in toluene solution: (1) before irradiation; (2) after (2×10^{-4}s) one-pulse irradiation by the light of a xenon (IFPP-7000) lamp; (3) 20 ms after switching off the pulse.

decayed during 80–250 ms at room temperature. In the case of the Zn^{II} complex **1** (no. 1 in Table 1) the long-wave absorption at 660 nm totally disappears within 80 ms after switching off the photolytic lamp pulse. For the Be complex **1** (no. 2 in Table 1) the decay of long-wave absorption at 608 nm occurs in *ca.* 20 ms. Much slower is the decay observed at the shorter-wave bands of these (and other listed in Table 1) complexes, see Figs. 1 and 2. Total decoloration in toluene solution at 25 °C requires 230 and 120 ms for, respectively, Zn^{II} (no. 1) and Be^{II} (no. 2) complexes. In both cases the spectrokinetic curves obtained by monitoring absorption at the maxima of different bands of the photocoloured forms diverge, each of these being of non-exponential character. These peculiarities of the thermal back reaction clearly indicate the formation of at least two isomers of the coloured species obtained by the irradiation of the solutions of complexes **1** and **2** possessing non-identical life-times. Such behaviour is in line with that of the photocoloured forms of 2*H*-chromenes,[12] spiropyrans[8,9] and spirooxazines[13] for which up to four spectrally-identified configurational and conformational isomers of **3b** thermally converting to **3a** at different rates were found to be formed after photocleavage of the C_{spiro}–O bond in **3a**.

Although no definite conclusion as to the nature of the photoisomers of **1** and **2** can be drawn on the grounds of the spectral data available, it seems justified that photodissociation of the M–O bond occurring in the first singlet excited state serves as the primary step of the photochromic reaction. The absorption of the photocoloured species of complexes **1** and **2** well matches that of the photoisomers of salicylaniline and salicylalkylimines[11,14] as well as loose ion-pairs formed by their anions with alkali metal counter-ions in polar solvents.[15] In both cases the spectral pattern is due to the species originating from cleavage of either H–O or M–O bonds. Cleavage of the M–N bonds in complexes **1** and **2** is known to occur readily in solution serving as one of the competitive pathways for the thermal inversion of configuration at a tetrahedral metal centre. However, in none of this

type of reaction were coloured intermediates observed.[1–3]

The photochromic behaviour of complexes **1** and **2** may now be explained by analogy with the mechanism of photochromic reactions of *N*-alkyl(aryl)salicylaldimines and spiropyrans, as shown in Scheme 1.



The intermediate **4** represents a structural analogue of the primary photoproducts of the excited-state proton-transfer reactions of salicylaniline and its congeners[14] as well as the s-*cis*-quinone allyde intermediate formed at the stage of C–O bond scission in **3**.[12] The intermediate **4** should possess the longest wave absorption and rapidly rearranges to a more stable conformer **5**. The estimated rate of the overall decay process in the dark back reaction is of the same order of magniture as that found for salicylaniline and the uranyl complex of its derivative.[10]

Compounds **1** and **2** display very high cycle-repeating durability, *i.e.* stability to photodecomposition. No measurable loss in intensity of the long-wave absorption of the coloured species was observed in toluene solution after 50 pulses (500 J) of a xenon lamp taken at 1–3 min intervals.

Pure bulk films of the complexes **1** and **2** in the solid amorphous state obtained by vacuum deposition (420–450 °C, 2×10^{-5} Torr) on a quartz surface showed, upon UV-irradiation, an irreversible photocoloration reaction, the spectral characteristics of the coloured species being similar to those observed in solution (Table 1).†

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† The compounds listed in Table 1 were prepared and purified as previously described.[2,3] UV-visible absorption spectra were recorded on a SPECORD M-40 spectrophotometer. Lamp-flash photoexcitation was performed by means of a xenon IFPP-7000 lamp (500 J, 2×10^{-4} s pulses) emitting in the spectral region of 230–1000 nm.